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MULTILAYER ALUMINUM OXYNITRIDE CAPACITORS FOR HIGHER ENERGY DENSITY, WIDE TEMPERATURE APPLICATIONS (PREPRINT)

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14. ABSTRACT
Capacitors are a pervasive technology in every military and commercial application. Increased performance and smaller size in capacitor devices have been the main focus of our research in the development of new dielectrics. A multilayer stacked rigid aluminum oxynynitride (AlaN) capacitor design concept has been developed to improve the energy density and high temperature capability of AlaN capacitors. This method consists of depositing alternating layers of dielectric and metal on a rigid substrate. A rigid substrate can withstand the stresses of the dielectric being coated on only a single side which eliminates the wrinkling problem of depositing AlaN on thin metal foil and metallized polymer substrates. The inherent surface roughness issue associated with commercially available polymers is no longer a concern as the surface finish of the substrate can be more easily controlled. Amorphous aluminum oxynitride films possess unique properties of high dielectric strength, high resistivity, low loss, high decomposition temperature, chemical inertness and good thermal conductivity. Dual DC pulsed magnetron reactive sputtering was employed to synthesize amorphous AlaN films on various substrates. Dielectric properties were compared for films developed with different process conditions. The properties were optimized with respect to the following input parameters: DC power, pulse frequency, total pressure, substrate temperature and reactive gas ratio. The effects on the dielectric constant, frequency dependence of capacitance, dissipation factor, resistivity, and breakdown strength of these films were measured using simple parallel plate capacitor test structures. Temperature dependent dielectric properties were evaluated from -200 °C to 400 °C.

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Introduction

High Power Density Capacitors

Capacitors are key components in all forms of electrical devices. Military systems utilize millions of capacitors and consider them key components due to their susceptibility for failure. Future needs for weapons systems and aircraft performance require the development of compact, high energy density capacitors for pulsed power and extreme environment applications. Current pulsed power applications are dominated by polymer film capacitors. Available state-of-the-art (SOTA) dielectric materials include polymer films such as polypropylene (PP), polyester (PET) and polyvinylidene fluoride (PVdF)[1]. Polymers are used for most AC applications because of their non-polar nature and low dielectric losses. Key drawbacks to polymer films include their low operating temperature, typically ~100°C[1], and their large volume-to-weight ratio, which compromises energy storage density.

Most polymers also have a dielectric constant (k) in the range of 2 – 4, although k for PVdF is from 10 – 12 [1]. These low k values make it difficult to obtain the high energy density required for future military applications. Polymer breakdown voltage is typically ~550 V/μm[1]. Energy density (u_v) depends linearly on dielectric constant (k) and on the square of the breakdown strength (E_B) of a capacitor as shown in Equation 1,

$$u_v = \tfrac{1}{2} k \varepsilon_o E_B^2 \qquad (1)$$

where ε_o is the permittivity of free space. Increasing the breakdown voltage increases the energy density more rapidly than increasing the dielectric constant. Current SOTA polymer dielectrics achieve material energy densities between 3 and 10 J/cc. Improved dielectric materials for capacitors are needed to meet the military's future power applications. Materials with a higher dielectric constant, greater dielectric breakdown strength and superior thermal stability are needed to improve capacitor performance to meet emerging needs.

Aluminum Oxynitride Dielectrics

Crystalline aluminum nitride (AlN) is a semiconductor with one of the largest known bandgaps (6.2 eV)[2,3] with dielectric strength between 400 and 550 V/μm[4] and thermal conductivity from 320 W/mK [3]. Amorphous AlN retains many of the crystalline properties and the insulating properties and high resistivity in conjunction with the high breakdown strength make amorphous AlN a desirable material for high density power applications. Thin AlN films have been deposited using a wide range of processes including MOCVD[5,6], RF and DC magnetron sputtering[4,7,8,9,10], and pulsed laser deposition[3,10]. Film structures from amorphous to epitaxial crystals have been obtained by varying deposition parameters and substrates[11]. Pulsed DC sputter deposition produces faster deposition rates than other deposition methods and also results in less substrate heating and thermal stressing of the films[9]. The aluminum target does not experience the same target poisoning that occurs during Al_2O_3 sputtering, making the AlN process easier to control and reproduce[8]. Thin amorphous Al_2O_3 films have shown breakdown strength ~500 V/μm[12]. Aluminum oxynitride deposition utilizing DC pulsed magnetron sputtering is a stable, repeatable process. Thin films deposited from this method show breakdown strengths ~600 V/μm[13,14].

Stacked Multilayer Capacitors

Multilayer capacitor configurations are a well established technology for increasing the energy density of a capacitor device. Multilayer construction can increase the energy density by up to ten times compared to conventional single layer capacitor fabrication[15]. The large increase in energy density comes from the removal of the inert, volume-filling carrier material. Further reduction of the metal layer thickness in the stack will additionally increase the energy density towards its theoretical limits. Thin film multilayered capacitors also reduce processing issues arising from the film stress and wrinkling associated with depositing thin dielectric films on very thin polymeric and foil substrates for rolled structures. Multilayer capacitors are also more compatible with surface mount technology than rolled capacitors. Multilayer devices do typically have a drawback with higher inductance and effective series resistance than single layer capacitors.

Experimental

Film Synthesis

Amorphous aluminum nitride films were deposited using a pulsed DC magnetron sputtering technique. The chamber was pumped to a base pressure less than $5x10^{-6}$ Torr before deposition. DC power was varied from 500 – 2000 W with pulse frequencies from 25 – 250 kHz. Films were deposited using pure nitrogen, nitrogen/oxygen and nitrogen/nitrous oxide gas mixtures with 99.999% pure aluminum sputter targets. Gas pressures ranged from 3 mTorr to 20 mTorr. Deposition conditions strongly influence the crystallinity of the films[16], but optical and secondary electron microscopy observation confirmed our films were amorphous under the deposition conditions examined. The target-to-substrate spacing was adjusted to influence substrate heating and film uniformity with an optimal distance of 5 inches used for the majority of the runs. The target was conditioned for 10 - 30 minutes before each run using argon plasma to remove contamination from the surface. Deposition times were adjusted to achieve ~5000 Å films. Thicknesses were verified using profilometry. Parallel plate capacitors were constructed by evaporating 3 mm diameter dots on the top surface of the deposited films through a shadow mask.

Multilayer Capacitor Fabrication

Multilayer capacitor structures were deposited using in-situ processing. The aluminum foil web handling system was utilized to position a shadow mask over the substrate. The pulsed magnetron system was employed to deposit aluminum metal contacts from an argon plasma and oxynitride dielectric layers from a nitrogen/oxygen gas mixture in the same chamber. The aluminum target was sputtered in argon with the shutter closed to remove the oxynitride from the surface between dielectric and metal depositions. Capacitors with one to seven dielectric layers were constructed.

Dielectric Property Evaluation

Capacitance and dissipation factors were measured as a function of frequency using an LCR meter. Multiple measurements were taken at each frequency and averaged for the capacitor. Several capacitors were tested on each film to confirm uniformity across the material. The dielectric constant was calculated using the average capacitance value at 1 kHz and the measured thickness for each film. The capacitance and dissipation factor were also measured at elevated and cryogenic temperatures. The dielectric breakdown strength was measured using an electrometer. Breakdown voltage was determined by applying a voltage stepped in regular increments to a capacitor for set time durations and measuring the resulting leakage current until film failure occurred.

Results and Discussion

Deposition Rate

Aluminum oxynitride thin films were deposited from nitrogen/oxygen and nitrogen/nitrous oxide reactive gas mixtures. It has bee shown that the addition of oxygen to a nitrogen plasma improve the dielectric properties of the resulting film[14]. The additional oxygen also has the downside of reducing the sputter deposition rate. Nitrous oxide (N_2O) is an alternative reactant to oxygen. The double bonded nitrogen in N_2O has a bond strength of ~ 450 kJ/mol compared to the triple bond strength of ~950 kJ/mol in N_2. It is also easier to break the nitrogen-oxygen bond in N_2O than the oxygen-oxygen bond in O_2[17]. The weaker bond strengths in N_2O result in a more reactive gas mixture with both oxygen and nitrogen present. Al_2O_3 is more thermodynamically favorable than AlN and both N_2O and O_2 provide sufficient excess oxygen in the plasma that the deposited film are primarily aluminum oxide, with a small (<10%) amount of nitrogen incorporated into the material. Figure 1 compares the deposition rate for films sputtered in N_2:N_2O and N_2:O_2 mixtures. The deposition rate is approximately two times higher in the N_2O environment that for the O_2 environment.

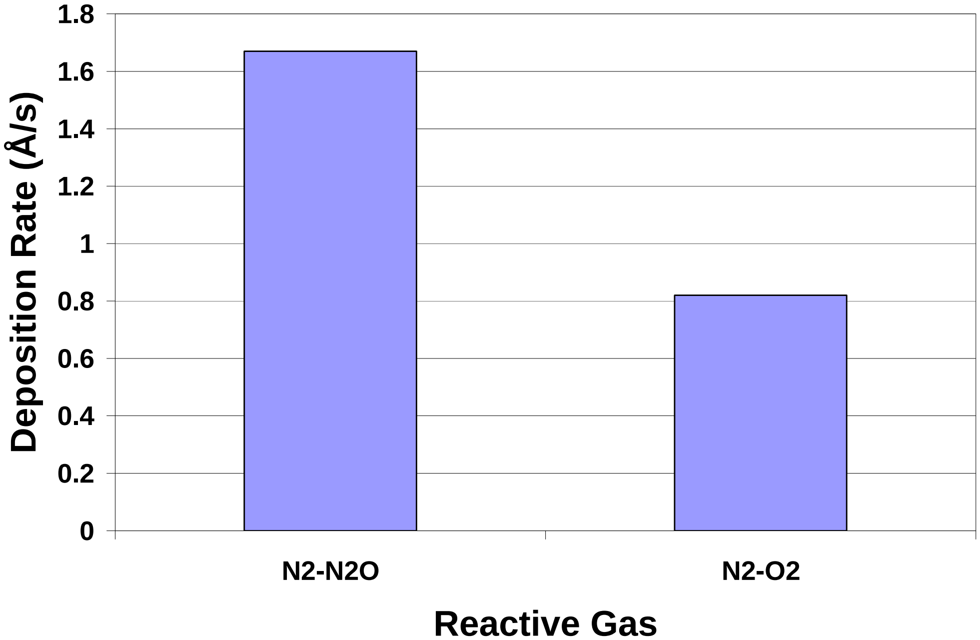

Figure 1. Deposition rate from N_2:N_2O and N_2:O_2 mixtures.

Dielectric Properties

The dielectric properties were also compared for films deposited with N_2:N_2O and N_2:O_2 combinations. Figure 2 plots the capacitance vs. frequency for capacitors grown with each of the reactive gas mixtures. In each case, the capacitance is stable with frequency from 20 Hz to 1 MHz. A dielectric constant between 8 and 9 is obtained for both formulations and differences in the capacitance observed in Fig. 2 are due to differences in film thickness resulting from the deposition rates. Dielectric breakdown strength is a critical parameter in obtaining high energy density and the dissipation factor is a key indicator of losses in the material. DC power and the reactive gas ratio are the primary inputs that influence the dissipation factor and the breakdown strength[14]. Optimal conditions for these parameters differed for N_2:N_2O and N_2:O_2 gas mixtures. The dissipation factor at 1 kHz was measured to be ~0.003 under the optimal deposition conditions for each mixture. Figure 3 is a plot of leakage current vs. applied voltage the same films shown in Fig. 2. Both films breakdown under equivalent applied fields, with the dielectric breakdown strengths ~550 V/µm.

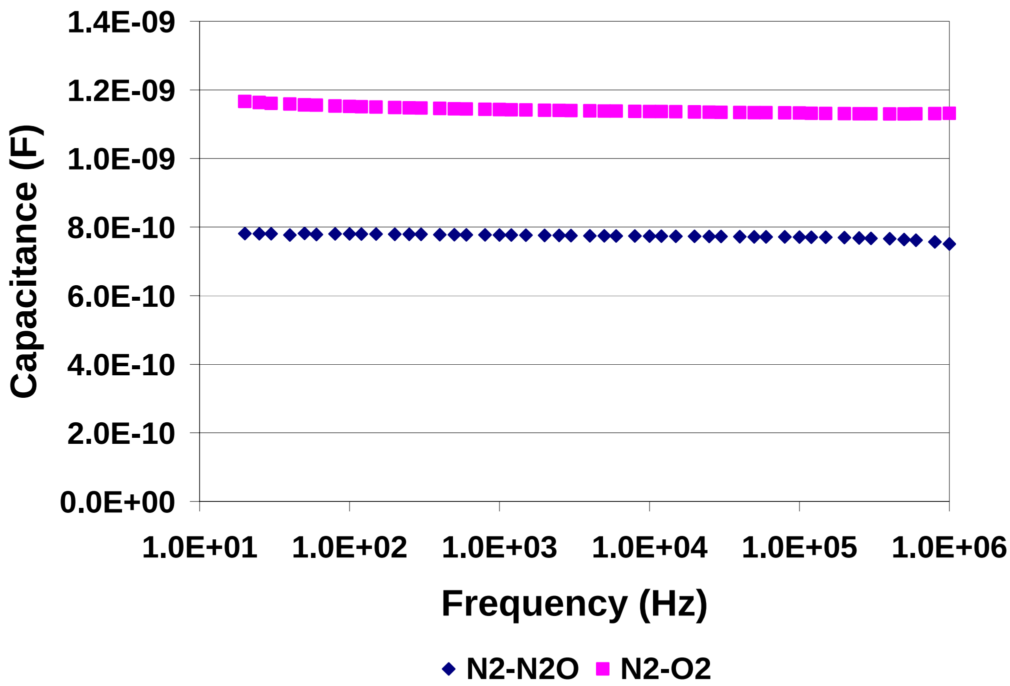

Figure 2. Capacitance vs. frequency for films deposited from N_2:N_2O and N_2:O_2 mixtures.

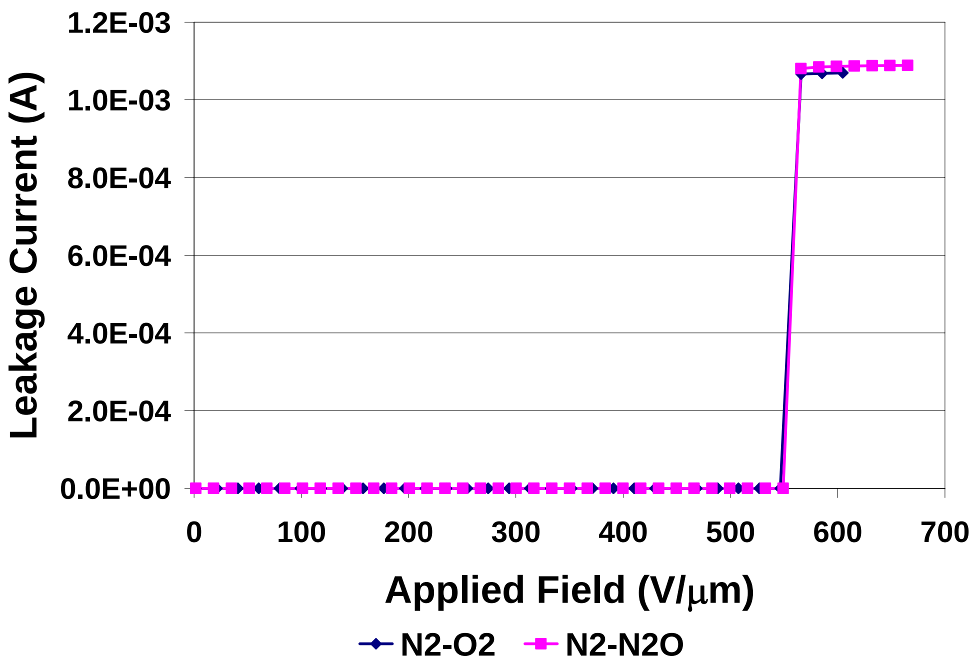

Figure 3. Breakdown strength for films deposited from N_2:N_2O and N_2:O_2 mixtures.

Multilayer Capacitors

Aluminum oxynitride multilayer capacitors were developed using pulsed DC magnetron sputtering with N_2:O_2 reactive gases. Figure 4 is a schematic cross-section of a simple three layer device. Multiple capacitors with one to seven layers were constructed by alternating the deposition of aluminum and AlON. Stepper motors were used to selectively position shadow masks in front of the substrate during metal and dielectric sputtering. Capacitance measurements were taken from an LCR meter and normalized for the capacitor area. Figure 5 plots the capacitance at 1 kHz vs. number of layers. The capacitance increased linearly with each additional dielectric layer, with a value of ~0.18 nF/mm for each layer. Based on a dielectric constant of 9, with a breakdown strength of 600 V/μm, the theoretical dielectric energy density for a 5000 Å film would be ~15 J/cc. The aluminum electrode layers were estimated to be between 100 Å and 500 Å thick depending on deposition time, and the energy density of the total multilayer structures was calculated using the metal thickness, a 5000 Å dielectric thickness, 300 V (600 V/μm) and the measured capacitance value. The energy density remains approximately independent of the number of layers in the device. Close comparison between the one layer devices and the six and seven layer devices suggest there may be some increase in the energy density with an increasing number of layers, but the spread in the data is too great for an authoritative conclusion. The average energy density determined from all of the capacitors examined is 14.1 J/cc, over 90% of the theoretical value.

Figure 4. Cross-sectional schematic of AlON multilayer capacitor.

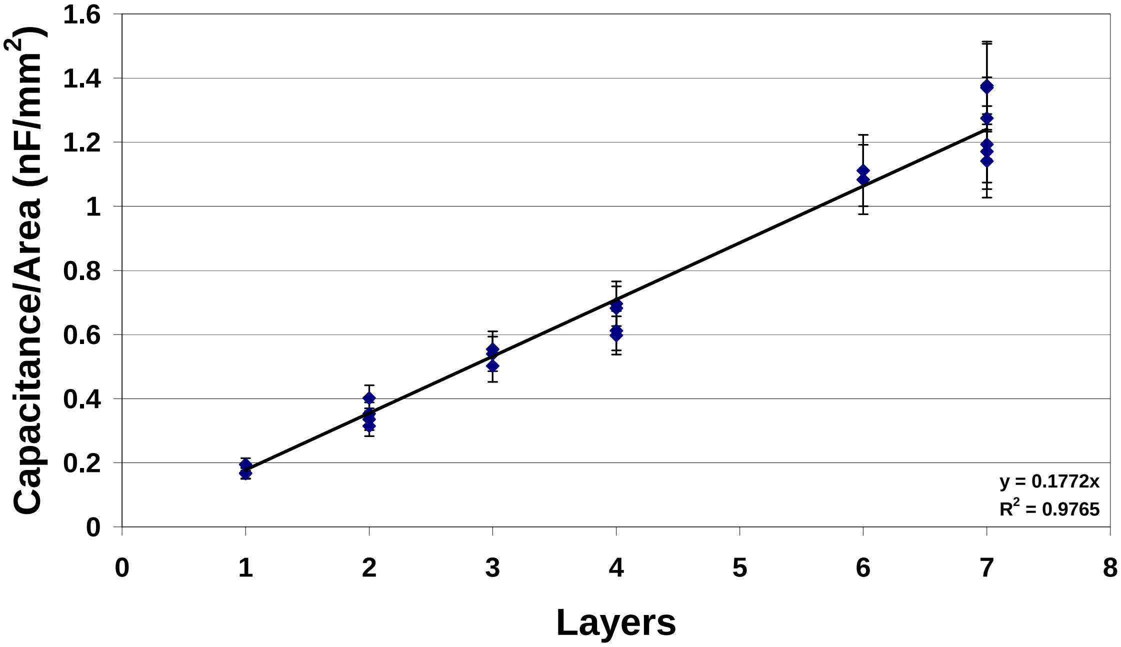

Figure 5. Capacitance vs. layer for multilayer capacitors.

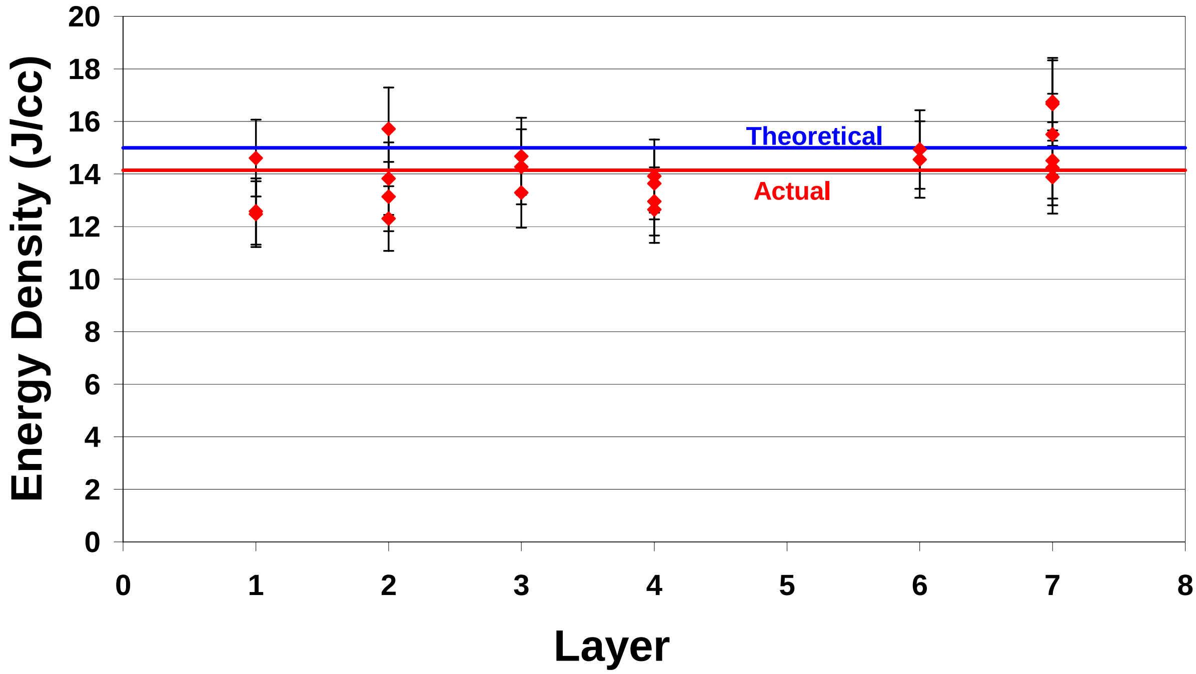

Figure 6. Energy density vs. layer for multilayer capacitors.

Thermal Properties

Temperature stability is another important parameter for capacitor performance under extreme conditions. Figure 7 depicts the capacitance vs. frequency for multiple temperatures under vacuum. The capacitance remains constant with frequency and is stable with increasing temperature to 300°C. As the temperature is increased above 300°C, the capacitance increases at low frequencies, while above 10 kHz no temperature effects are observed up to 400°C. The capacitance also remains stable under cryogenic conditions, with no variations observed down to -200°C. The differences in the capacitance between the elevated and cryogenic temperatures in Fig. 7 are due to differences in dielectric thickness between the samples measured. When capacitors are heated in ambient air, the capacitance at low frequency begins to increase around 200°C but still remains constant at high frequencies.

The dissipation factor is more temperature dependent than the capacitance. Under vacuum, significant increases in DF begin above 200°C while in air increases are observed around 150°C. No change in the dissipation factor is observed under cryogenic conditions. The difference between film performance in vacuum and in ambient air at elevated temperatures may be related to the atmospheric boundary layer present on the surface. Interactions with particulates in the atmospheric boundary layer over the top electrode may begin to alter the electric field as the temperature increases. The boundary layer is more pronounced in atmospheric air compared to vacuum environment and the temperatures effects are seen at lower temperatures. The temperature effects on both capacitance and dissipation factor are reversible. The original values are reacquired after returning the material back to room temperature and are stable after multiple temperature cycles. The high and low temperature values are also repeatably obtained on each temperature cycle. This indicates the observed capacitance and dissipation shifts are not caused by a chemical reaction, but by reversible interactions between the atmosphere and the surface.

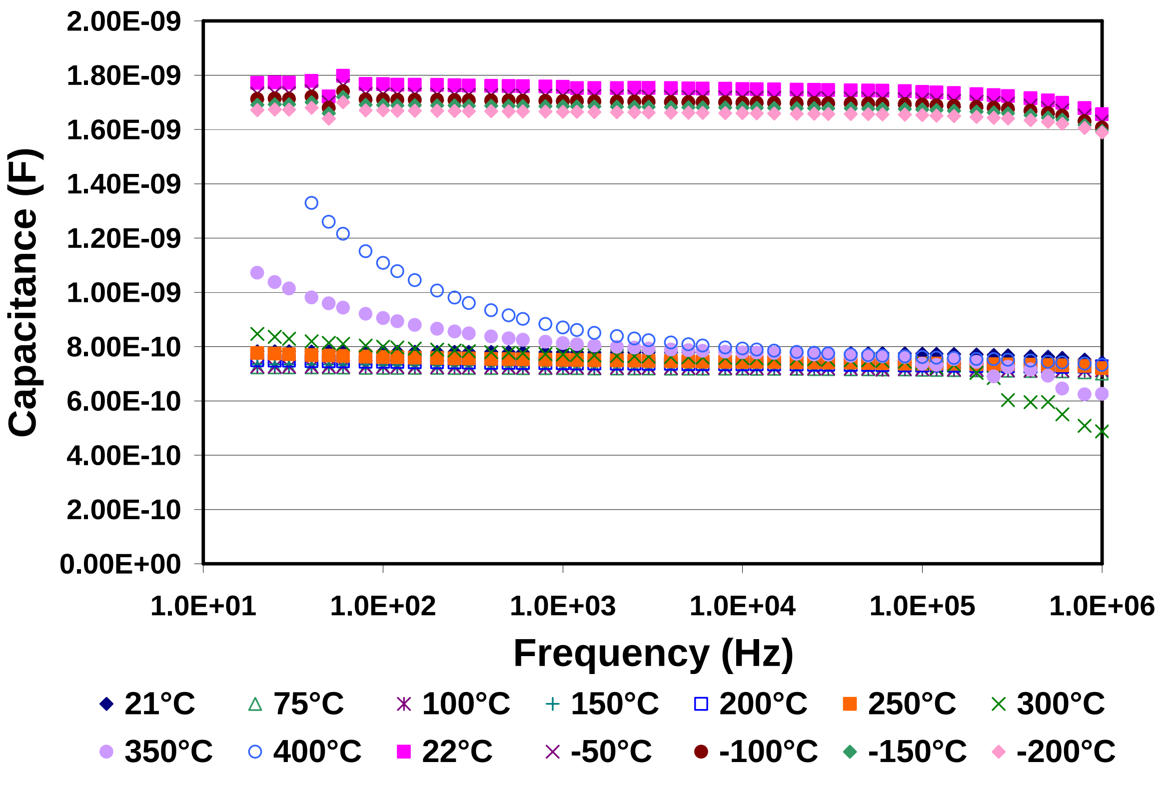

Figure 7. Effects of temperature on capacitance.

Conclusions

Aluminum oxynitride dielectrics for high energy density capacitors applications have been deposited using a pulsed DC magnetron sputtering technique. Multilayer capacitor structures have been developed using in-situ deposition of alternating aluminum and aluminum oxynitride layers. Stacked devices showed a linear increase in capacitance with increasing layers and a capacitance of ~0.18 nF/mm has been obtained for devices with one to seven dielectric layers. The energy density of the multilayer devices is independent of the number of layers, with a value of ~14.1 J/cc, greater than 90% of the theoretical energy density for aluminum oxynitride materials. Comparisons between films sputtered in N_2:N_2O and N_2:O_2 reactive gas environments reveal films grown in both mixtures exhibit similar dielectric properties after optimization. A dielectric constant from 8-9 and a dissipation factor of 0.003 are obtained at 1 kHz for optimized deposition conditions using both N_2O:N_2 and N_2:O_2. The N_2:N_2O mixture does produce a deposition rate twice that of N_2:O_2 under conditions for optimal dielectric properties. The capacitance remains stable with temperature from -200°C to 400°C. The dissipation factor is more temperature sensitive and begins demonstrating temperature deviations above 200°C. The temperature effects are reversible and films regain their as-deposited properties when returned to room temperature.

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